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SPECIALTY PAPER FOR INK JET RECORDING

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[There are no amendments to this patent.]

Abstract

Objective

To improve specialty paper for ink jet recording.

Constitution

An ionic group-containing unsaturated polyester is subjected to aqueous dispersion and slow coagulation for granulation, followed by a hollowing treatment depending on the water absorbing/dewatering effect realized by means of heating and a crosslinking treatment performed by means of seed polymerization to obtain [particles of] a hollow crosslinked polyester resin having internal pores. Then, an ink-absorbing layer comprising the obtained particles and a binder is formed on the surface of a support paper.

Claim

A specialty paper for ink jet recording having an ink-absorbing layer coated on a support characterized by, the absorbing layer containing polyester resin particles with internal pores.

Detailed explanation of the invention

[0001]

Industrial application field

The present invention pertains to specialty paper for ink jet recording.

[0002]

Prior art

Ink jet recording systems which print characters or images by jetting fine ink drops onto recording paper are widely used for industrial marking or OA printers because they have low noise and the parts are easy to miniaturize. Although both oil-based and water-based inks can be used for ink jet recording, water-based inks are mainly used for OA because of environmental reasons. The biggest weakness of the ink jet recording system is possible clogging of the ink jet heads when the ink dries. To solve this problem, a humectant, such as a glycol or glycerin, is added to the water-based ink. Moreover, the humectant added for improving the reliability of the jet heads causes a delay in drying of the ink printed on the recording paper.

[0003]

In order to solve this problem from the side of the recording paper, an ink-absorbing layer is formed on the surface of the recording paper that accelerates drying by quickly absorbing the liquid components in the ink and suppresses bleeding to improve the recording image quality. The ink jet recording paper is usually classified into "normal paper " and "specialty paper." The "normal paper " is not really normal paper. Instead, it is a type of special paper which is size pressed to a certain degree such that the normal paper feel is not deteriorated. In the case of the normal paper type, the ink absorbability is controlled by the types and amounts of the extender pigment and the sizing agent and by the surface processing agent used in the size pressing treatment. Examples of the extender pigment that can be used include talc, kaolin, calcined kaolin, silica, calcium carbonate, etc. Examples of the sizing agent that can be used include rosin size, alkyl ketene dimer, size-pressed starch, polyvinyl alcohol, etc. If the expectations of ink jet recording cannot be met by the size pressing treatment, it is necessary to use the "specialty paper" with a porous coating layer formed on the surface of the recording paper. The porous coating layer is composed of a pigment, binder, and assistant. A porous material with a low refractive index is used as the pigment in order to obtain a high ink absorbability and coloring density. More specifically, amorphous silica, hydrated alumina, soft calcium carbonate, magnesium carbonate, or talc can be used. Among them, amorphous silica is the most preferred. A water-soluble binder resin, such as polyvinyl alcohol or polyvinylpyrrolidone, can be used as the binder. By using the aforementioned ink-absorbing porous coating, the formation of feather rings, which occur as the ink bleeds in a whisker pattern along the pulp fibers of the paper, can be inhibited, and the roundness of the ink drops can be improved. Consequently, the quality of the recorded images can be improved.

[0004]

Problems to be solved by the invention

The ink-absorbing layer of the conventional specialty paper for ink jet recording has been explained above. The conventional technology, however, has the following problems. The ink-absorbing layer must be thick in order to absorb the jetted ink layer alone. However, the mechanical strength of the recording paper becomes low as the thickness of the absorbing layer is increased. Also, although amorphous silica has high absorbability, it is difficult to prepare a high-concentration coating solution which is then used to form the absorbing layer. As a result, a multilayer coating is required in order to form a thick absorbing layer, which leads to a significant increase in manufacturing costs. The thickness of the absorbing layer can be reduced in the case when ink is absorbed by both the ink-absorbing layer and the paper used as the support. In order to prevent bleed-through, etc. by stopping the ink near the surface of the support paper, it is necessary to perform a sizing treatment on the support paper in advance, using calcined kaolin, silica, soft calcium carbonate, etc. As a result, manufacturing costs increase. Also, compared with normal paper, since a large amount of inorganic pigment is used in this case, the recording paper becomes heavy, and the stiffness of the paper disappears. Also, the ability to write on the paper with pencil as well as other applications in business use become poor. In addition, the silanol groups on the surface of the silica particles may deteriorate the light fastness or the storability by means of photoactivity. In order to solve the aforementioned problems, the present inventors performed extensive research on specialty paper for ink jet recording which can accelerate the ink drying speed and realize a high image durability. As a result of this research work, the present invention was achieved.

[0005]

Means to solve the problems

That is, the present invention provides a specialty paper for ink jet recording having an ink-absorbing layer coated on a support characterized by, the absorbing layer containing polyester resin particles having internal pores.

[0006]

The inner pore-containing polyester particles are mainly comprised of a crosslinked resin obtained by performing polymerization after adding 5-99 wt% of a vinyl-based monomer to 1-95 wt% of a polyester resin (preferably, containing ionic groups in the range of 20-2000 eq/ton) obtained by condensing a polyhydric alcohol component and a polybasic carboxylic acid component, preferably 5 mol% or greater of an unsaturated polybasic carboxylic

acid. The volume-average particle size D is in the range of 0.5-100 μm. There are one or plural independent pores filled with gas or liquid or pores which are connected to each other with fine holes inside the particles. The porosity is in the range of 1-99 vol%. The volume-average particle size D of the particles used in the present invention is in the range of 0.5-100 μm, preferably in the range of 1-50 μm, more preferably in the range of 2-25 μm, even more preferably in the range of 2-15 μm, or most preferably in the range of 2-9 μm. If the volume-average particle size is too small, binding of the particles becomes difficult. On the other hand, if the volume-average particle size is too large, the particles become impractical as an additive for a coating material. The particle size distribution of the particles used in the present invention should be such that the content of the particles with a size in the range of 0.5D-2.0D is 70 wt% or greater, preferably 80 wt% or greater, more preferably 85 wt% or greater, or most preferably 90 wt% or greater. In another way to describe this, the particle size range of 70 wt% or greater of the particles is preferably 0.6D-1.8D, more preferably 0.7D-1.5D, even more preferably 0.8D-1.3D, or most preferably 0.9D-1.2D. Also, the variation coefficient, a value obtained by dividing the standard deviation by the average value, should be 30% or less, preferably 20% or less, more preferably 15% or less, or most preferably 10% or less.

[0007]

The particles of the present invention have one or plural independent internal pores. In the present invention, the porosity must be in the range of 1-99 vol% in both cases. The porosity is a value obtained by dividing the volume of the pores inside the particles by the apparent volume of the particles. The porosity is preferably in the range of 2-98 vol%, more preferably in the range of 5-95 vol%, even more preferably in the range of 10-95 vol%, or most preferably in the range of 20-90 vol%. The pores are filled with a gas or liquid. Preferable examples of the gas include air, nitrogen, carbon dioxide, etc. A preferable example of the liquid is water. Although the particles of the present invention have no special limitation in this regard, the apparent specific weight of the dry particles, that is, the apparent specific weight when the particles are filled with a gas, is preferably in the range of 0.1-1.3, more preferably in the range of 0.2-1.2, or most preferably in the range of 0.5-1.0.

[0008]

The particles of the present invention are mainly composed of a crosslinked resin obtained by performing polymerization after adding 5-99 wt% of a vinyl-based monomer to 1-95 wt% of a polyester resin. In this case, the content of the polyester resin used is preferably in

the range of 10-90 wt%, more preferably in the range of 20-80 wt%, or most preferably in the range of 30-70 wt% of all of the resin components. The polyester resin used in the present invention comprises a polybasic carboxylic acid and a polyhydric alcohol. Examples of the polybasic carboxylic acids that can be used for the polyester resin include terephthalic acid, isophthalic acid, o-phthalic acid, 1,5-naphthalenedicarboxylic acid, 2,6-naphthalenedicarboxylic acid, 9,10-anthracenedicarboxylic acid, 9,10-anthracenedipropionic acid, diphenic acid, sulfoterephthalic acid, 5-sulfoisophthalic acid, 4-sulfophthalic acid, 4-sulfonaphthalene-2,7-dicarboxylic acid, 5-(4-sulfophenoxy)isophthalic acid, sulfoterephthalic acid, and/or their metal salts, ammonium salts, and other aromatic dicarboxylic acids,

p-hydroxybenzoic acid, p-(hydroxyethoxy)benzoic acid, and other hydroxyaromatic carboxylic acids, succinic acid, adipic acid, azelaic acid, sebacic acid, dodecanedicarboxylic acid, and other aliphatic dicarboxylic acids,

fumaric acid, maleic acid, itaconic acid, mesaconic acid, citraconic acid, and other aliphatic unsaturated polybasic carboxylic acids,

phenylenediacrylic acid and other aromatic polybasic carboxylic acids,

hexahydrophthalic acid, tetrahydrophthalic acid and other alicyclic acids,

trimellitic acid, trimesic acid, pyromellitic acid, and other trihydric or greater polybasic carboxylic acids.

In the present invention, it is also possible to use a monocarboxylic acid together with the polybasic carboxylic acid. It is preferred to use an aromatic monocarboxylic acid. Examples of the aromatic monocarboxylic acids that can be used include benzoic acid, chlorobenzoic acid, bromobenzoic acid, p-hydroxybenzoic acid, naphthalenecarboxylic acid, 4-methylbenzoic acid, 3-methylbenzoic acid, salicylic acid, thiosalicylic acid, phenylacetic acid, and their lower alkyl esters, sulfobenzoic acid monoammonium salt, sulfobenzoic acid monosodium salt, cyclohexyl aminocarbonylbenzoic acid, n-dodecylaminocarbonylbenzoic acid, t-butylbenzoic acid, naphthalenecarboxylic acid, anthracenecarboxylic acid, t-butylnaphthalenecarboxylic acid, etc., among which t-butylbenzoic acid is more preferred. The content of the aromatic monocarboxylic acid is in the range of 2-25 mol%, preferably in the range of 5-20 mol%, or more preferably in the range of 8-16 mol% with respect to the acid component.

[0009]

In the present invention, an unsaturated aliphatic polybasic carboxylic acid must be used in an amount of 5 mol% or greater with respect to the polybasic carboxylic acid component. Preferable examples of the unsaturated polybasic carboxylic acid that can be used in the present

invention include fumaric acid and maleic acid, among which fumaric acid is more preferable. The amount of unsaturated polybasic carboxylic acid used must be 5 mol% or greater, preferably in the range of 20-50 mol%, or more preferably in the range of 30-50 mol% with respect to the acid components.

[0010]

Examples of the polyhydric alcohols that can be used for the polyester resin include aliphatic polyhydric alcohols, alicyclic polyhydric alcohols, aromatic polyhydric alcohols, etc.

Examples of the aliphatic polyhydric alcohols that can be used include ethylene glycol, propylene glycol, 1,3-propanediol, 2,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, diethylene glycol, dipropylene glycol, 2,2,4-trimethyl-1,3-pentanediol, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, and other aliphatic diols, trimethylolethane, trimethylolpropane, glycerin, pentaerythritol, and other triols and tetraols.

Examples of the alicyclic polyhydric alcohols that can be used include 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, spiroglycol, hydrogenated bisphenol A, ethylene oxide adducts and propylene oxide adducts of hydrogenated bisphenol A, tricyclodecanediol, tricyclodecanedimethanol, etc.

Examples of the aromatic polyhydric alcohols that can be used include paraxylene glycol, metaxylene glycol, orthoxylene glycol, 1,4-phenylene glycol, ethylene oxide adducts of 1,4-phenylene glycol, bisphenol A, ethylene oxide adducts and propylene oxide adducts of bisphenol A, etc.

Also, examples of polyester polyols that can be used include lactone-based polyester polyols obtained by performing ring-opening polymerization for lactones, such as -caprolactone.

In addition, similar to the carboxylic acids, aliphatic alcohols, aromatic alcohols, alicyclic alcohols, and other monoalcohols can also be used.

[0011]

The glass transition temperature of the polyester resin used in the present invention should be 40C or greater, preferably 45C or greater, more preferably 50C or greater, even more preferably 60C or greater, or most preferably 70C or greater. If the glass transition temperature is too low, blocking tends to occur during handling or storage, making it difficult to handle the obtained powder. The number-average molecular weight of the polyester resin used in the present invention is preferably in the range of 100-20,000, more preferably in the range of

2000-5000, or most preferably in the range of 3000-4000.

[0012]

In the present invention, it is preferred that the polyester resin contain 20-2000 eq/ton of ionic groups. Examples of the ionic groups that can be used include sulfonate, carboxyl, sulfate, phosphate, phosphonate, phosphinate, or their ammonium salts, metal salts, or other anionic groups, or primary to tertiary amine groups or other cationic groups, among which alkali metal sulfonate groups and ammonium carboxylate groups are preferable. It is preferred that these ionic groups be copolymerized with the polyester or introduced to the end of the polymer. Examples of the polybasic carboxylic acids containing alkali metal sulfonate groups that can be copolymerized with the polyester include sulfoterephthalic acid, 5-sulfoisophthalic acid, 4-sulfophthalic acid, 4-sulfonaphthalene-2,7-dicarboxylic acid, 5-[4-sulfophenoxy]isophthalic acid, and/or their salts. Metal sulfonate groups can also be introduced to the end of the polymer by jointly using the metal salts of sulfobenzoic acids. Examples of the salts include salts of ammonium-based ions as well as, Li, Na, K, Mg, Ca, Cu, Fe, Ni, Co, Al, etc., among which the salts of K or Na are particularly preferable. The carboxyl groups can be added to the end of the polymer by introducing a polybasic carboxylic acid, such as trimellitic acid, into the system at the end of the polymerization of the polyester. They can also be exchanged with carboxylate groups by being neutralized with ammonia, sodium hydroxide, etc. The content of ionic groups must be in the range of 20-2000 eq/ton, preferably in the range of 20-500 eq/ton, or more preferably in the range of 50-200 eq/ton with respect to the polyester resin.

[0013]

Examples of the vinyl-based monomers that can be used to crosslink the polyester resin in the present invention include alkyl (meth)acrylates, methoxyethyl (meth)acrylate, hydroxyethyl (meth)acrylate, phenyl (meth)acrylate, cyclohexyl (meth)acrylate, glycidyl (meth)acrylate, and other (meth)acrylic esters with 1-10 carbon atoms in the alkyl groups, methyl vinyl ketone, phenyl vinyl ketone, methyl isopropenyl ketone, and other unsaturated ketones, vinyl formate, vinyl acetate, vinyl propionate, vinyl butanoate, and other vinyl esters, methyl vinyl ether, ethyl vinyl ether, propyl vinyl ether, and other vinyl ethers, vinyl halides and vinylidene halides, acrylamide and its alkyl-substituted compounds, styrene, divinylbenzene, alkyl-substituted styrenes, halogen-substituted styrenes, allyl alcohols and their esters or ethers, acrolein, methacrolein, and other vinyl aldehydes, acrylonitrile, methacrylonitrile, vinylidene cyanide, and other vinyl monomers, as well as acrylic acid, methacrylic acid, fumaric acid,

maleic acid, itaconic acid, and other unsaturated carboxylic acids and their salts, vinylsulfonic acid, acrylsulfonic acid, p-styrenesulfonic acid, and other unsaturated hydrocarbon sulfonic acids and their salts, phosphate esters having double bonds and their salts, pyridine, vinylpyrrolidone, vinylimidazole, vinylcarbazole, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, etc. In addition to these, siloxanes, lactones, lactams, epoxy compounds, and other ring-opening polymerization monomers can be used jointly.

[0014]

There is no special limitation on the reaction initiator. Any well-known initiator can be used. Examples include benzoyl peroxide, p-chlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide, capryryl peroxide, lauryl peroxide, acetyl peroxide, methyl ethyl ketone peroxide, cyclohexanone peroxide, bis(1-hydroxycyclohexyl peroxide), hydroxyheptyl peroxide, t-butyl hydroperoxide, p-menthane peroxide, cumene hydro[peroxide], 2,5-dimethylhexyl-2,5-dihydro peroxide, di-t-butylperoxide, dicumyl peroxide, 2,5-dimethyl-2,5-di(peroxybenzoate), t-butyl perbenzoate, t-butyl peracetate, t-butyl peroctoate, t-butyl peroxyisobutyrate, di-t-butyl di-perphthalate, succinic acid peroxide, and other organic peroxide-based reaction initiators, azoisobutyro nitrile, deoxy benzoyl phenyl acetaldehyde, phenyl pyroglucose, pinacol acid derivative, and other reaction initiators. Examples of the catalyst promoters that can be used include those that are cobalt-based, vanadium-based, manganese-based, tertiary amine-based, quaternary ammonium-based, mercaptan-based, etc.

[0015]

In the following, the detailed method used for obtaining the hollow crosslinked polyester resin of the present invention will be explained. There are two basic methods which can be used to obtain the hollow crosslinked polyester resin particles of the present invention: the method in which hollow polyester particles are first formed, followed by crosslinking with a vinyl monomer after the particles have swelled, and the method in which crosslinking is performed at the same time the hollow polyester particles are formed.

[0016]

The following concerns the method for obtaining hollow polyester resin particles.

1) An example of the method in which the polyester particles are made hollow at the same time they are formed is described below:

the hollow particles are obtained by forming a W/O/W type emulsion by adding water

after dissolving an ionic group-containing polyester resin in a water-soluble organic compound.

2) Examples of the method in which solid polyester particles are made hollow by a post-treatment are listed below:

a) the solid particles of an ionic group-containing polyester resin are heated to a temperature above the glass transition point in an aqueous medium;

b) a water-soluble organic compound is added to an aqueous dispersion of ionic group-containing polyester resin particles, followed by azeotropic boiling to remove the water-soluble organic compound; and

c) a solvent is added to an aqueous dispersion of ionic-group containing polyester resin particles to swell the particles, followed by making the particles hollow when the particles are being dried using the spray dry method, etc.

The solid polyester particles used in each of methods 2a-b can be obtained by milling and classifying an ionic group-containing polyester resin. However, it is preferred to use polyester resin particles obtained by the water-based granulating method to be described later. The hollow particles of a polyester resin can be obtained by crosslinking with a vinyl monomer after swelling the obtained hollow particles.

[0017]

1) An example of the method in which crosslinking is performed at the same time the hollow polyester particles are formed is described below.

In this method, the solid particles of an ionic group-containing polyester resin are swollen in an aqueous medium [before adding the] vinyl monomers. In the mean time, the particles are heated to a temperature above the glass transition temperature. In this way, the particles can be made hollow at the same time crosslinking is performed. As described above, the solid polyester particles used in this method can be obtained by milling and classifying an ionic group-containing polyester resin. However, it is preferred to use polyester resin particles obtained by using the water-based granulating method to be described later.

[0018]

In the following, the method for forming polyester particles using the water-based granulating method will be explained. The ionic group-containing polyester resin used in the present invention is water-dispersible. The aqueous microdispersion of the ionic group-containing polyester resin of the present invention can be manufactured using any conventional method. That is, the microdispersion can be prepared by adding water to a mixture

obtained by mixing an ionic group-containing polyester resin and a water-soluble organic compound in advance at a temperature in the range of 50-200C or by adding a mixture of an ionic group-containing polyester resin and a water-soluble organic compound to water, followed by stirring at a temperature in the range of 40-120C. Or, the dispersion method can involve adding the ionic group-containing polyester resin to a mixture of water and a water-soluble organic compound, followed by stirring at 40-100°C. Examples of the water-soluble organic compounds that can be used include ethanol, butanol, isopropanol, ethyl cellosolve, butyl cellosolve, dioxane, tetrahydrofuran, acetone, and methyl ethyl ketone. Although it is not preferred to use a surfactant jointly, there is no special limitation. The average particle size of the aqueous microdispersion obtained in this way is usually in the range of 0.01-1.0 μm. By adding an electrolyte to the aqueous microdispersion of the ionic group-containing polyester resin under such conditions that the ionic group-containing polyester resin can be plasticized, the microdispersion particles are guided to a slow coagulation region where the polyester particles can be formed as a result of particle growth.

[0019]

Examples of the electrolytes that can be used in the present invention include sodium sulfate, ammonium sulfate, potassium sulfate, magnesium sulfate, sodium phosphate, sodium dihydrogen phosphate, disodium hydrogen phosphate, ammonium chloride, calcium chloride, cobalt chloride, strontium chloride, cesium chloride, barium chloride, nickel chloride, magnesium chloride, rubidium chloride, sodium chloride, potassium chloride, sodium acetate, ammonium acetate, potassium acetate, sodium benzoate, and other inorganic or organic water-soluble salts. The concentration of the electrolyte is preferably in the range of 0.01-2.0 mol/L, more preferably 0.1-1.0 mol/L, or most preferably in the range of 0.2-0.8 mol/L if a monovalent electrolyte is used. The amount of the electrolyte added should be less if a polyvalent electrolyte is used. In the present invention, the purpose can be well realized by either adding the electrolyte to the system beforehand or adding the electrolyte afterwards. Preferably, however, better polyester resin particles can be obtained by "performing electrolysis after adding an electrolyte precursor." Examples of the electrolyte precursors that can be used include salts which are difficult to dissolve at low temperature but are easy to dissolve at high temperature, and compounds which can be decomposed and electrolyzed under certain conditions of pH, temperature, pressure, light irradiation, etc. Esters of amino alcohols and carboxylic acids are preferable electrolyte precursors that can be used in the present invention. Since such esters have amino groups, they are water-soluble, and their aqueous solutions are alkaline. When the

alkaline aqueous solution is heated, the ester bonds are hydrolyzed to generate an amino alcohol and a salt of a carboxylic acid. The amino groups actually function as primary to tertiary ammonium groups. Preferable amino alcohols that can be used in the present invention include aminoethanol, 1,3-aminopropanol, 1,4-aminobutanol, dimethylaminoethanol, 1,3-dimethylaminopropanol, diethylaminoethanol, diethylaminopropanol, etc. Examples of the carboxylic acids that can be used include benzoic acid and its derivatives, salicylic acid, phenylacetic acid, acetic acid, propionic acid, butanoic acid, octanoic acid, decanoic acid, dodecanoic acid, lauric acid, stearic acid, acrylic acid, methacrylic acid, etc. In the present invention, it is preferred to use esters in any combination of the aforementioned amino alcohols and carboxylic acids as the electrolyte precursors.

[0020]

The polyester particles obtained in this way are virtually spherical and have a sharp particle size distribution. Also, they are capable of high-temperature dispersed dyeing at a high concentration. The polyester particles obtained in this way can freely control the volume-average particle size D in the range of 1-100 μm (depending on the electrolyte concentration, temperature, and time). The particle size distribution is such that the content of particles with a particle size in the range of 0.5D-2.0D is 80 wt% or greater and the variation coefficient is 30% or less. The particles are in a virtually spherical shape with a sphericity (minor diameter/major diameter) of 0.8 or greater. Compared with the vinyl-based polymer particles obtained by means of suspension polymerization, etc., the specificity of the particles of the present invention is not only limited in the diversity of the properties of the polyester resin but also reflected in the shape and particle size distribution of the polyester particles. For the normal suspension-polymerized particles, the particle size distribution is broad, and the variation coefficient is 30% or greater. In the present invention, the content of particles with a particle size in the range of 0.5D-2.0 D can reach 80 wt% or greater, preferably 85 wt% or greater, more preferably 90 wt% or greater, or most preferably 95 wt% or greater by adjusting the granulating conditions. Also, the variation coefficient can reach 30% or less, preferably 20% or less, more preferably 15% or less, or most preferably 10% or less. In addition, the average sphericity (minor diameter/major diameter) can reach 0.8 or greater, preferably 0.85 or greater, more preferably 0.9 or greater, or most preferably 0.95 or greater. In this case, the variation coefficient refers to the value obtained by dividing the standard deviation by the average value.

[0021]

Preferably, in the present invention, the polyester particles obtained in this way are used as seed particles to generate crosslinked hollow particles. The polyester particles obtained using the water-based granulating method have a very high dispersion stability in aqueous media. They do not coagulate even after undergoing a swelling operation procedure involving a vinyl monomers or a heat treatment performed above the glass transition temperature. The crosslinked hollow resin particles obtained in this way can maintain the particle size distribution of the polyester seed particles. The content of particles with a particle size in the range of 0.5D-2.0D can reach 80 wt% or greater, preferably 85 wt% or greater, more preferably 90 wt% or greater, or most preferably 95 wt% or greater by adjusting the granulating conditions. Also, the variation coefficient can reach 30% or less, preferably 20% or less, more preferably 15% or less, even more preferably 10% or less, or most preferably 7% or less. In the present invention, it is most preferred to use the method in which a heat treatment is performed above the glass transition temperature. A preferable heat treatment temperature is in the range from the glass transition temperature of the polyester resin to 200C. The temperature is more preferably 140C or less, even more preferably 100C or less, or most preferably 90C or less. The concentration of the electrolyte is preferably 0.2 mol/L or less, more preferably 0.1 mol/L, or most preferably 0.05 mol/L.

[0022]

A different type of aqueous dispersion can be introduced to the polyester resin particles of the present invention by means of heterocoagulation during the particle growth process. It is also possible to use a polyester microdispersion colored by a dye, etc. In this way, the particles can be dyed and become functional. Examples of the aforementioned different type of aqueous dispersion include pigments, latex, carbon black, and other dispersions. After the obtained particles are washed and dewatered, they are dried and obtained as a dry powder using the freeze drying method, spray-drying method, flow-drying method, or vacuum-drying method. Of course, if necessary, the particles can also be used in the original state, that is, the dispersed state in an aqueous medium. The content in the internal pores can be replaced.

[0023]

The conventional internal pore-containing polyester particles are used to prepare a coating solution together with binders and assistants if necessary. The coating solution is coated and dried on a support to form an absorbing layer. Examples of the so-called coating binders that can be used include modified starch, carboxymethylcellulose, hydroxyethylcellulose,

methylcellulose, casein, gelatin, natural rubber, and other natural or semisynthetic polymers, polyvinyl alcohol, polyvinylpyrrolidone, isoprene, neoprene, polybutadiene, and other polydienes, polybutene, polyisobutylene, polypropylene, polyethylene, and other polyalkenes, vinyl halides, vinyl acetate, styrene, (meth)acrylic acid, (meth)acrylic ester, (meth)acrylamide, methyl vinyl ether, and other vinyl-based polymers or copolymers, polyesters, polyurethanes, polyamides, styrene/butadiene, methyl methacrylate/butadiene/maleic acid and other synthetic rubber latexes, and other synthetic polymers. It is preferred to use a water-soluble binder in the present invention.

[0024]

The amount of binder used can be adjusted in a range such that there is no adverse effect on the function of the hollow porous particles. The amount of binder used is usually 500 wt% or less, or preferably in the range of 0.01-200 wt% of the particles. Various types of assistants can be added. Examples of the assistants include calcium carbonate, talc, kaolin, titanium oxide, aluminum hydroxide, zinc oxide, fine urea/formaldehyde resin particles, fine melamine particles, fine guanamine resin particles, and other inorganic or organic pigments, dyes used for controlling the color tone and whiteness, UV absorbents and antioxidants used for improving the storability, as well as dispersants, wetting agents, and defoaming agents used for realizing coating suitability. For the specialty paper for ink jet recording of the present invention, if the absorbing layer is thinner than 1 μm, the expected effect cannot be realized. Therefore, the thickness of the absorbing layer should be 3 μm or larger, or preferably in the range of 5-50 μm. If the average particle size of the hollow porous resin particles that form the absorbing layer is smaller than 1 μm, there is almost no absorbing effect. On the other hand, if the average particle size is larger than 50 μm, the surface characteristics will be deteriorated. Consequently, one of the preferable embodiments of the present invention is to adjust the average particle size of the hollow particles to about 1-20 μm.

[0025]

In order to improve the writing property, it is also possible to add various types of assistants to the absorbing layer. Examples of the assistants include heavy or light calcium carbonate, talc, clay, natural or synthetic silicic acid, aluminum hydroxide, zinc oxide, urea resin, aldehyde resin powder, and other inorganic or organic pigments, UV absorbents, antioxidants, antistatic agents, mold-releasing agents, lubricants, etc. The support can be normal paper, synthetic paper, synthetic resin film, etc. The so-called normal paper includes paper

which is mainly composed of a cellulose pulp and is manufactured in the conventional manner with a paper strength reinforcer, sizing agent, fixing agent, inorganic or organic fillers added as well as paper in which the surface property has been improved by size pressing oxidized starch, etc. in the paper or by forming a precoating layer mainly composed of clay or other pigments. It is particularly preferred to use art paper, coated paper, cast-coated paper, or other paper with a smooth surface. For synthetic paper, it is preferred to a polyester-based or polypropylene-based synthetic paper. It is particularly preferred to use a polyester-based synthetic paper because it has excellent adhesion with the binder resin. In order to control the adhesivity, barrier property, smoothness, hiding property, etc., it is also possible to form an undercoat layer or laminate or bond a thin film base material before or after forming the absorbing layer on the support.

[0026]

Since the specialty paper for ink jet recording of the present invention obtained in this way has good ink-absorbing characteristics, ink can be dried quickly. Also, since there is no bleeding, high-quality characters and images can be printed. In addition, since the added particles are well adhered to the binder resin and the support paper, the paper has excellent mechanical strength and is stiff and light. Also, the paper has a good pencil writing property and satisfactory business suitability.

[0027]

In the following, the present invention will be explained in more detail with reference to application examples. The present invention, however, is not limited to these application examples.

Application examples

[Polymerization of polyester resin (A1)]

45 parts by weight of dimethyl terephthalate,

45 parts by weight of dimethyl isophthalate,

9 parts by weight of sodium 5-sulfoisophthalic acid dimethyl ester,

20 parts by weight of ethylene glycol,

260 parts by weight of an ethylene oxide adduct of bisphenol A, and

0.1 part by weight of tetrabutoxy titanate

were added to an autoclave equipped with a thermometer and a stirrer, followed by 120 min of heating performed at 120-220C to carry out an ester exchange reaction. Then, the

temperature of the reaction system was lowered to 180C, followed by adding

58 parts by weight of fumaric acid and

0.1 part by weight of hydroquinone, and

the reaction was carried out at 200C for 60 min. After that, the temperature of the reaction system was raised to 220-240C, and the reaction was continued for 60 min with the pressure of the system adjusted to 1-10 mm Hg. As a result, a copolymerized polyester resin (A1) was obtained. According to NMR analysis, the composition of the obtained copolymerized polyester resin (A1) was as follows.

Terephthalic acid: 23 mol%

Isophthalic acid: 23 mol%

Fumaric acid: 50 mol%

Sodium 5-sulfoisophthalic acid: 4 mol%

Ethylene glycol: 25 mol%

Ethylene oxide adduct of bisphenol A: 75 mol%

The glass transition temperature was 61C. The acid value was 0.08 [mg/KOH g]. The number-average molecular weight derived by means of GPC was 4500. The sodium sulfonate group equivalent derived by means of fluorescent X-ray analysis of elemental S was 98 meq/kg.

[0028]

[Polymerization of polyester resin (A2)]

196 parts by weight of maleic anhydride,

700 parts by weight of a propylene oxide adduct of bisphenol A, and

1 part by weight of hydroquinone

were added to an autoclave equipped with a thermometer and a stirrer, followed by feeding nitrogen gas into the reaction system to form an inactive atmosphere. Then, 0.05 part by weight of dibutylthin oxide was added, and the reaction was carried out at 200C, obtaining a polyester resin (A2). The glass transition temperature of the obtained copolymerized polyester resin (A2) was 57C. The acid value was 24.1 [mg/KOH g]. The number-average molecular weight derived by means of GPC was 1800.

[0029]

Manufacture of polyester aqueous microdispersion

After 300 parts by weight of polyester resin (A1), 150 parts by weight of methyl ethyl ketone, and 140 parts by weight of tetrahyhdrofuran were dissolved at 80C, 680 parts of water at

a temperature of 80C were added to obtain an aqueous microdispersion of the copolymerized polyester resin with a particle size of about 0.1 μm. Then, the mixture was added to a distillation flask, and distillation was performed until the distillation fraction temperature reached 100C. After cooling and removing the solvent, water was added to obtain a polyester aqueous microdispersion (B1) with a solids content of 30%.

[0030]

After 100 parts of butanol were added to 300 parts of polyester (A2) and dissolved at 90°C, the temperature was decreased to 80°C. Then, a 1N ammonia aqueous solution was added in an amount equivalent to the acid value of the copolymerized polyester. After stirring was performed for 30 min while the temperature was maintained at 80°C, 500 parts of water with a temperature of 80°C were added, forming an aqueous microdispersion of the copolymerized polyester. The obtained aqueous microdispersion was added to a flask for distillation, where distillation was performed until the distillation fraction temperature reached 100°C, followed by cooling. After the solution was removed, a aqueous microdisperison (B2) of copolymerized polyester with a solids content of 30% was obtained.

[0031]

Manufacture of polyester particles

300 parts by weight of the polyester aqueous microdispersion (B1) were added to a 4-necked 1-L separatory flask equipped with a thermometer, a condenser, and stirring vanes, followed by raising the temperature to 80C. Then, 40 parts by weight of a 20 wt% aqueous solution of dimethylaminoethyl methacrylate were added over 60 min (0.2 mol/L), followed by continuous stirring with the system maintained at 80C for 300 min. The conductance in the system rose from about 1 mS to 25 mS, while the pH dropped from 10.8 to 6.7. In this way, it was confirmed that the added dimethylaminoethyl methacrylate was almost completely hydrolyzed and became dimethylaminoethanol and a salt of methacrylic acid. The copolymer with a particle size on the submicron order and existing in the polyester aqueous microdispersion grew as composite particles over time to from spherical polyester particles (C1) with an average particle size D of 5.2 μm derived using the Coulter counter method and having 98% or greater of particles with a particle size in the range of 0.5D-2.0D. Then, the experiment was carried out in the same way using different raw materials under different conditions, obtaining polyester particles (C2) with an average particle size D of 3.4 μm and having 96% or greater of particles with a particle size in the range of 0.5D-2.0D.

[0032]

Formation of hollow particles

After the polyester particles (C1) were dewatered, washed, and redispersed in water, they were diluted with deionized water to obtain a polyester particle aqueous dispersion with the solids content adjusted to 5%. 1000 parts by weight of the polyester aqueous dispersion were added to a separatory flask and stirred gently, while the temperature of the system was raised to 90C. 30 min later, 2000 parts by weight of deionized water were added for cooling. The obtained particles were dewatered and washed in an absorbing device and were redispersed in water to obtain hollow polyester particles (D1). Then, hollow particles (D2) were obtained from polyester particles (C2) in the same way.

Crosslinking

The aqueous dispersion of the hollow polyester particles (D1) was diluted with deionized water to obtain a polyester particle aqueous dispersion with the solids concentration adjusted to 5%. 1000 parts by weight of the polyester aqueous dispersion were added to a separatory flask and stirred gently. At the same time, 50 parts by weight of distilled styrene containing 1 wt% benzoyl peroxide were added dropwise, followed by 30 min of stirring. Then, the temperature of the system was raised to 80C, and the reaction was carried out continuously for 300 min. After the system was cooled to room temperature, the obtained particles were dewatered and washed in an absorbing device and then vacuum dried, forming dry hollow crosslinked polyester particles (E1). The average particle size D of the obtained particles was 6.6 μm. The content of particles with a size in the range of 0.5D-2.0D was 98% or greater. The variation coefficient was 8.7%, and the porosity was 54%. The porosity was derived from the density difference of the particles. Then, hollow crosslinked particles (E2) with an average particle size D of 4.3 μm, content of particles with a particles size in the range of 0.5D-2.0D of 97% or greater, variation coefficient of 9.2%, and porosity of 45% were obtained from hollow particles (D2) in the same way.

[0033]

Coating

Application Example 1

200 parts of an aqueous polyester resin Toyobo Vylonal MD 1200 (solids concentration: 34%) were added as a binder to 100 parts (solids content) of the obtained internal

pore-containing hollow crosslinked polyester particles (E1) to prepare a coating solution (solids concentration: 30%) used for the absorbing layer. The coating solution was coated and dried on a commercially available high-quality paper (basis weight: 81 g/m^2, paper compression: 80 μm) such that the dry weight became 10 g/m^2. As a result, a specialty paper for ink jet recording (F1) was obtained.

[0034]

Application Example 2

Then, a specialty paper for ink jet recording (F2) was obtained in the same way using hollow crosslinked particles (E2).

[0035]

Application Example 3

(F3) was obtained in the same way except that a synthetic paper Yupo FPG-80 (product of Oji Yuka Synthetic Paper Co., Ltd.) made of polypropylene was used as the support instead of the high-quality paper, and hollow crosslinked polyester particles (E1) were used.

[0036]

Application Example 4

(F4) was obtained in the same way except that a polyester-based synthetic paper, Crisper 1G1111 (product of Toyobo Co., Ltd.), was used as the support instead of the high-quality paper, and hollow crosslinked polyester particles (E1) were used.

[0037]

Application Example 5

(F5) was obtained in the same way except that a polyester-based synthetic paper, Crisper 1G1212 (product of Toyobo Co., Ltd.), was used as the support instead of the high-quality paper, and hollow crosslinked polyester particles (E1) were used.

[0038]

Comparative Example 1

A specialty paper for ink jet recording (F6) was obtained in the same way as described in Application Example 1 except that 85 parts by weight of amorphous silica particles and 15 parts by weight of talc powder were used in the coating solution for the absorbing layer instead of the

hollow polyester particles.

[0039]

Comparative Example 2

A specialty paper for ink jet recording (F7) was obtained in the same way as described in Application Example 1 except that 15 parts by weight of swollen hollow particles (F-30 Microspheres, product of Matsumoto Yushi Seiyaku K.K.) and 85 parts by weight of titanium oxide powder were used in the coating solution for the absorbing layer instead of the hollow polyester particles.

[0040]

Comparative Example 3

A specialty paper for ink jet recording (F8) was obtained in the same way as described in Application Example 1 except that 100 parts by weight of the particles (C1) obtained in Application Example 1 before hollowing and crosslinking were used in the coating solution for the absorbing layer instead of the hollow polyester particles.

[0041]

Evaluation

A quality comparison test was conducted for the 8 types of specialty paper for ink jet recording obtained above. The results are listed in Table 1. More specifically, an ink jet printer MJ-500 (product of Seiko-Epson Co., Ltd.) and ink of the same quality were used to perform test printing for 70 mm x 70 mm solid patterns and Chinese characters on the recording paper obtained in the application examples and the comparative examples in a standard environment of 25C and 60% RH. A MacBeth densitometer (RD-914) was used to measure the recording density of the solid patterns. The test print with Chinese characters was touched with fingers 10 sec after printing, and the drying rate was evaluated depending on the presence/absence of ink contamination on the fingers. The test print with Chinese characters was observed visually with a 25X loupe to evaluate the reproducibility and bleeding of the dots. The evaluation was made based on the following standards.

(Evaluation standards)

A: No bleeding, the roundness of the dots is good.

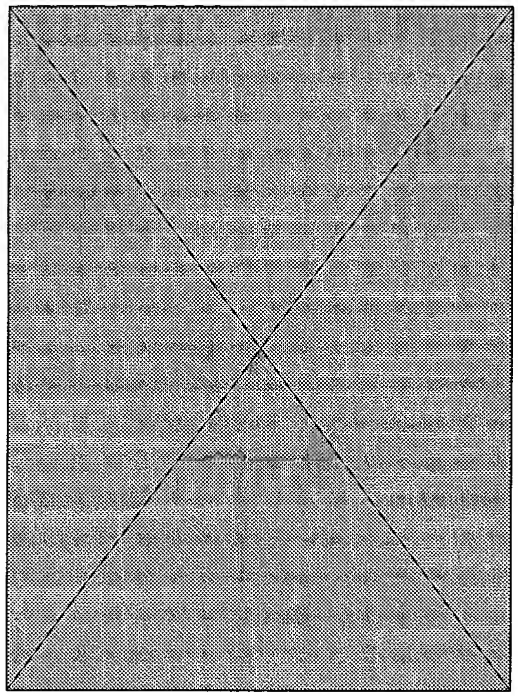
B: Although a little bleeding is observed, it causes no problem in practical application.

C: Bleeding is conspicuous and causes poor roundness of the dots.

D: Due to bleeding, dots lack roundness, and there is no practicality at all.

[0042]

Table 1



Key:
1 Application Example
2 Comparative Example
3 Recording density
4 Dry
5 Image quality

[0043]

Effect of the invention

As can be seen from the results of Table 1, the specialty paper for ink jet recording obtained in the application examples of the present invention have a high drying rate and can be used to obtain recorded images with high density and perfect dot roundness.

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(57)【要約】	(57) [Abstract]
【目的】　インクジェット記録用紙の改良。	[Objective]　Improvement of inkjet recording paper form.
【構成】　イオン性基含有不飽和ポリエステルを水分散し、緩凝集させることにより粒子化し、加熱による吸脱水作用による中空化処理とシード重合による架橋をへて内部に空孔を有する中空架橋ポリエステルを得る。次いで支持紙表面に得られた粒子とバインダーからなるインク吸収層を設ける。	[Constitution]　Water dispersion it does ionic group-containing unsaturated polyester, to particle it converts gentle bycohering, hollowing due to suction dewatering effect due to heating and it obtains thehollow crosslinked polyester which possesses void in interior crosslinking due to theseed　polymerization by way of. ink-absorbing layer which consists of particle and binder which are acquirednext in supporting paper surface is provided.
【特許請求の範囲】	[Claim(s)]
【請求項１】　支持体上にインク吸収層が被覆されてなるインクジェット記録用専用紙において、該吸収層が、内孔を有するポリエステル樹脂粒子を含有することを特徴をするインクジェット記録用専用紙。	[Claim 1]　Ink-absorbing layer being covered on support, in specialty paper for inkjet recording whichbecomes,　said absorbing layer, containing polyester resin particle which possesses　inner hole thespecialty paper　for inkjet recording which does feature.
【発明の詳細な説明】	[Description of the Invention]
【０００１】	[0001]
【産業上の利用分野】本発明はインクジェット記録用専用紙に関するものである。	[Field of Industrial Application] This invention is something regarding specialty paper for inkjet recording.
【０００２】	[0002]
【従来の技術】微細なインク滴を記録紙に吹き付けるこ	[Prior Art] Printing or ink jet recording which does image forma